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This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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INVENTOR(S)

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
Krzysztof	Matyjaszewski	Pittsburgh, PA

Additional inventors are being named on the 1 *separately numbered sheets attached hereto*

TITLE OF THE INVENTION (500 characters max)

The Preparation of Functional (Co)Poly(tetrazoles)

Direct all correspondence to: **CORRESPONDENCE ADDRESS**

☐ Customer Number:

OR

☑ Firm or Individual Name	Carl P. B. Mahler, II				
Address	Carnegie Mellon University Innovation Transfer Center				
Address	4615 Forbes Avenue, Suite 302				
City	Pittsburgh	State	PA	Zip	15213-3890
Country	USA	Telephone	412.268.4387	Fax	412.268.7395

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SIGNATURE Carl P. B. Mahler, II

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TYPED or PRINTED NAME Carl P. B. Mahler, II

TELEPHONE 412.268.4387

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PROVISIONAL APPLICATION COVER SHEET
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INVENTOR(S)/APPLICANT(S)

Given Name (first and middle [if any])	Family or Surname	Residence (City and either State or Foreign Country)
Nicolay V.	Tsarevsky	Pittsburgh, PA

Number 1 of 1

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TITLE:

The Preparation of Functional (Co)Poly-tetrazoles

INVENTORS

Krzysztof Matyjaszewski and Nicolay V. Tsarevsky

TECHNICAL FIELD OF THE INVENTION

This invention is directed towards the preparation and use of oligo/polymeric species with attached tetrazole functionality. The attached tetrazole functionality can comprise telechelic tetrazole functionality, site specific tetrazole functionality, tetrazole functionality dispersed along a polymer backbone or polymer segments comprising attached tetrazole functionality. The oligo/polymeric species with attached tetrazole functionality can further comprise functionality derived from other monomer units in the oligo/polymeric species. The oligo/polymeric species can comprise a free standing material or a composite material wherein the oligo/polymeric material can be attached to an organic or an inorganic curved or flat surface. The functional (co)poly-tetrazoles are prepared by converting an acrylontrile monomer unit in a polymer first prepared by a controlled polymerization process to the tetrazole.

BACKGROUND OF THE INVENTION

Polymers with attached tetrazazole functionality have been prepared by the (co)polymerization of various vinyltetrazole monomers or by interaction of

polyacrylonitrile with sodium azide and ammonium chloride however, these polymers have not been prepared using a controlled polymerization process. Controlled radical polymerization (CRP) processes have been described in three ACS Symposium Series edited by Professor Matyjaszewski. [*ACS Symp. Ser.* Vol. *685,* **1998;** Vol. *768,* **2000**; *and* Vol. *854,* **2003**.] The use of a controlled radical polymerization process for the preparation of an oligo/polymeric material allows control over the molecular weight, molecular weight distribution of the (co)polymer and further it allows one to exercise molecular control over the topology, composition and functionality of a polymeric material. The topology can be controlled allowing the preparation of linear, star, graft or brush copolymers, formation of networks or dendritic or hyperbranched materials and can include such materials grown from any type of solid surface. Composition can be controlled to allow preparation of homopolymers, periodic copolymers, block copolymers, random copolymers, gradient copolymers, and graft copolymers. Functionality can be placed wherever desired on the oligo/polymer structure including side-functional groups, end functional groups providing homo- or hetero-telechelic materials or can comprise site specific functional groups, or multifunctional groups distributed as desired within the structure. The functionality can be dispersed functionality or can comprise functional segments. Since a controlled radical polymerization can be employed to prepare such materials then the composition of the polymer can comprise a wide range of radically copolymerizable monomers thereby allowing the bulk or surface properties of a material to be tailored to the application. Such control is now available for the preparation of oligo/polymeric materials further

comprising a tetrazole functionality and thereby permits the preparation of materials with controlled degrees of activity and selectivity in tetrazole based chemistry.

We exemplify this novel approach to tetrazole based polymers by preparing a series of 5-vinyltetrazole containing polymers by initial preparation of a series of polymers, including a hompolymer, a block copolymer, a star copolymer, a random copolymer and a tethered copolymer each containing acrylonitrile monomer units through ATRP followed by conversion of some or all of the nitrile functionality to a tetrazole ring.

ATRP is one of the most successful controlled/"living" radical processes (CRP) developed and has been thoroughly described in a series of co-assigned U.S Patents and Applications, U. S. Patent Nos. 5,763,546; 5,807,937; 5,789,487; 5,945,491; 6,111,022; 6,121,371; 6,124,411; 6,162,882; 6,407,187; 6,512,060; 6,538,091; 6,541,580; 6,624,262; 6,624,263 6,627,314; and U.S. Patent Applications 09/359,359; 09/534,827; 09/972,056; 10/034,908; 10/289,545 and 10/456,324 all of which are herein incorporated by reference, and has been discussed in numerous publications by Matyjaszewski as co-author and reviewed in several publications.

A living polymerization process is a chain growth process without or with an insignificant amount of chain breaking reactions, such as transfer and termination reactions. Controlled/living polymerization, herein "controlled polymerization", is a chain growth process that under controlled polymerization conditions provides effective control over the chain growth process to enable synthesis of polymers with molecular weight control and narrow polydispersities or molecular weight distributions. Molecular weight control is provided by a process having a substantially linear growth in molecular

weight of the polymer with monomer conversion accompanied by essentially linear semilogarithmic kinetic plots, in spite of any occurring terminations. Polymers from controlled polymerization processes typically have molecular weight distributions, characterized by the polydispersity index ("PDI"), of less than or equal to 2. The PDI is defined by the ratio of the weight average molecular weight to the number average molecular weight, M_w/M_n. More preferably in certain applications, polymers produced by controlled polymerization processes have a PDI of less than 1.5, and in certain embodiments, a PDI of less than 1.3 may be achieved.

Polymerization processes performed under controlled polymerizations conditions achieve these properties by consuming the initiator early in the polymerization process and, in at least one embodiment of controlled polymerization, an exchange between an active growing chain and dormant polymer chain is equivalent to or faster than the propagation of the polymer. A controlled radical polymerization ("CRP") process is a process performed under controlled polymerization conditions with a chain growth process by a radical mechanism, such as, but not limited to, atom transfer radical polymerization, stable free radical polymerization, specifically, nitroxide mediated polymerization, reversible addition-fragmentation transfer/degenerative transfer/catalytic chain transfer radical systems. A feature of controlled radical polymerizations is the existence of an equilibrium between active and dormant species. The exchange between the active and dormant species provides a slow chain growth relative to conventional radical polymerization, but all polymer chains grow at the same rate. Typically, the concentration of radicals is maintained low enough to minimize termination reactions. This exchange, under appropriate conditions, also allows the quantitative initiation early

in the process necessary for synthesizing polymers with special architecture and functionality. CRP processes may not eliminate the chain breaking reactions, however, the chain breaking reactions are significantly reduced from conventional polymerization processes.

Polymers produced under controlled polymerization conditions have a degree of polymerization that may be determined from the ratio of the amount of consumed monomer to the initiator, a polydispersity close to a Poisson distribution and functionalized chain ends. The level of control attained in a particular polymerization process is typically monitored by analyzing the kinetics of the polymerizations, the evolution of molecular weights, polydispersities and functionalities with conversion.

The initiator for a CRP can be attached to any physical surface including particles of any size and flat surfaces. In this manner functional particles or functional surfaces can be prepared. When only partial coverage of a surface is employed an array of functional segments on a surface can be formed.

To exemplify the procedure acrylonitrile has been incorporated into homopolymers, random copolymers, statistical copolymers, linear block copolymers, star block copolymers graft copolymers, brush copolymers and grafted from a particle surface using ATRP. These polymers display controlled molecular parameters are precursors for (co)polymers comprising tetrazole functionality thereby facilitating the preparation of materials that will allow known tetrazole based chemistry to be conducted in addition to providing materials for new applications.

NEED FOR THE INVENTION

Tetrazole is used as an activator in the synthesis of oligonucleotides for solid phase chemical synthesis of DNA fragments however the repetitive nature of the process requires multiple purification steps.

Tetrazole is frequently used in the synthesis of pharmaceuticals such as the preparation of tetracyclic tetrahydroquinoline inhibitors of serine proteases as antithrombotic agents however purification of the products is costly.

US Patent 6,598,901 describes that tetrazoles can be used as the gas generating agent for air bag and air bag apparatus a safe stable polymer would be advantageous in this application.

With the preparation of tetrazole containing polymers with controlled molecular parameters new applications for tetrazole containing materials can be developed such as information storage media, biological screening test media, stimulii responsive media and supported media for tetrazole based chemistries.

Traditional procedures for the direct preparation of tetrazoles in polymer backbones have recently been reviewed by Kizhnyaev, [Kizhnyaev, V. N.; Vereshchagin, L. I. *Russian Chemical Reviews* **2003**, *72*, 143-164] and described in; DE4211521 where the copolymerization of 2H-tetrazole with vinyl monomers provided homogeneous, reaction-processable polymers which are easily handled during processing. The copolymers, e.g., graft copolymers prepared from acrylonitrile, styrene, polybutadiene, and 5-phenyl-2-(4-vinylphenyl)-2H-tetrazole or 2-methyl-5-(4-vinylphenyl)-2H-tetrazole, are described as being useful alone or in blends [e.g., with poly(butylene terephthalate)] for the preparation of extruded articles showing high impact strength, high heat deformation temperature, and good chem. resistance.

DE4211522 described that similar polymers, based on vinyl-aromatic monomer(s), 2H-tetrazole(s) with vinyl:phenyl substituent(s), and polydiene graft base are useful in preparation of a polymer membrane, useful for ultrafiltration, dialysis etc.

Whereas, DE4222953 described the preparation of post-modifiable copolymers by emulsion copolymerization of styrene, acrylonitrile, and 2-methyl-5-(4-vinylphenyl)-2H-tetrazole that are processable by standard thermoplastic methods but could be modified by UV irradiation o provide surface crosslinking for improved impact and tensile strength. I.e. low level of tetrazole functionality are incorporated by copolymerization and used to initiate a grafting to or a crosslinking reaction.

US 3397186 describes triaminoguanidinium salts of 5-vinyltetrazole polymers which were prepared by copolymerization and are useful as rocket fuel binders.

Stille also described copolymerization of vinyl tetrazoles [Stille, J. K.; Gotter, L. D. *Kinet. Mech. Polyreactions, Int. Symp. Macromol. Chem., Prepr.* **1969**, *1*, 131-134; Stille, J. K.; Chen, A. T. *Macromolecules* **1972**, *5*, 377-384.] which allowed thermal crosslinking of copolymers containing dipolarophiles and the tetrazoles as nitrile imine dipol precursors.

The homopolymer of 2-(4-ethenyl)phenyl-5-phenyl-2H-tetrazole and its copolymers with styrene and acrylonitrile were prepared by Darkow, R.; Hartmann, U.; Tomaschewski, G. *Reactive & Functional Polymers* **1997**, *32*, 195-207. The solution behavior of the tetrazole-containing polymers is dependent on the H-bond participation of tetrazole rings and by hydrophobic interactions between monomer groups. [Annenkov, V. V.; Kruglova, V. *Journal of Polymer Science, Part A: Polymer Chemistry* **1993**, *31*, 1903-1906.]

The other approach to polymers containing tetrazole functionality, direct modification of polymers containing acrylonitrile functionality, has received much less attention. A recent paper on the synthesis of poly(5-vinyl tetrazole) by polymer-analogous conversion of polyacrlonitrile notes that the only prior discussion was in US 3096312.[Gaponik, P. N.; Ivashkevich, O. A.; Karavai, V. P.; Lesnikovich, A. I.; Chernavina, N. I.; Sukhanov, G. T.; Gareev, G. A. *Angewandte Makromolekulare Chemie* **1994**, *219*, 77-88.] US 3096312 provides conditions for conversion of polyacrylonitrile to poly(5-vinyltetrazole) by heating with NaN3 and NH4Cl in HCONMe2 for 24 hrs. at 120-5 Deg. Copolymers of acrylonitrile with styrene, Me methacrylate, or vinyl acetate similarly yield copolymers of 5-vinyltetrazole.

Another patent that describes preparation of a polytetrazoles is US 3350374 describes the preparation of copolymers of hydroxytetrazoles and hydrazide oximes. These polymers were prepared by modification of another precursor polymer. The title polymers are prepared from poly(hydroxamic acids) by treatment with SOCl2, giving poly(hydroxamyl chloride), which was then treated with hydrazine, giving the poly(hydrazide oxime). Treatment with NaNO2 and HCl gives a poly(azide oxime), which then rearranges to poly(hydroxytetrazole). The products are used as ion exchangers and explosives. The process is described as being less dangerous than the polymerization of a vinyltetrazole but again the initial polymers were not prepared by a controlled polymerization process and were therefore unable to be tailored to meet the requirements of property selective applications. Indeed in all prior publications and discussions the copolymer had been prepared by standard polymerization processes therefore no control over any molecular parameters was possible.

The high energy characteristics of tetrazole polymers, their relative stability, low toxisity and evolution of a large volume of neutral gas upon decomposition make polymers and copolymers based on vinyltetrazole promising components for gunpowders, explosives and propellants.

Taking into account high complex-forming ability of tetrazoles with heavy metal ions in aqueous media supported tetrazole polymeric species could find use as easily separated media that are additionally efficient adsorbents for solution of environmental problems or isolation of precious metals.

Unsubstituted poly-(C-vinyltetrazoles) manifest acidic properties and enter into interpolymeric reactions with natural high molecular weight compounds, which determines their anticoagulant properties. Quaternary salts exhibit the opposite effect: they bind heparin in the circulating blood and thus favor blood coagulation. The sodium salt of poly(5-vinyltetrazole) is a polyelectrolyte endowed with pronounced antiinflamatory and aseptic properties accelerates wound healing and suppresses cicatrisatation.

These benefits, and others listed below, provide an incentive for the preparation of polytetrazole (co)polymers with controlled functionality, topology, and composition providing solubility in diverse media and ease of separation as desired.

BRIEF DESCRIPTION OF INVENTION

Polymers or polymer modified surfaces comprising tetrazole functionality have a multiplicity of uses. Control over the distribution of the tetrazole functionality can

improve the performance of the material in many applications including addition of tetrazole functionality to any solid support; either an organic based support such as a crosslinked polystyrene resin or an inorganic support as exemplified below by grafting from SiO_2. The level of control now available in the preparation of oligo/polymers materials containing tetrazole functionality will be exemplified by the initial preparation of homopolymers and block copolymers comprising a polyacrylonitrile segment or a styrene/acrylonitrile copolymer segment. The polyacrylonitrile block or statistical styrene/acrylonitrile copolymer block can be directly prepared as a bulk or solution processable material or can be directly grafted to a substrate or can be attached to the substrate via a hydrophilic or hydrophobic spacer that will permit any material in a contacting solution to freely interact with the tetrazole functionality. For many applications macrobeads are be better for separation than nanocolloids and in such situations spacers can assist is ensuring good contact between the functional material and the desired reactant. By control over spacer length and composition and distribution of the attached tetrazole functionality one can modify the distribution of the attached tetrazole functionality in the contacting medium and allow close approach of a reactant such as DNA to the attached tetrazole functionality thereby promoting controlled DNA synthesis in a readily separable solid/liquid reaction medium.

Continuing to use DNA synthesis as an exemplary target reaction another route to a readily separable reaction medium now feasible through use of a CRP to prepare the tetrazole precursor polymer is to prepare a material with tetrazole functionality that can additionally exhibit a lower solution critical temperature (LCST) thereby allowing

homogeneous solution reaction between the tetrazole and the contacting reactant at one temperature while allowing solid/lquid separation to be conducted at a lower temperature.

Another route to readily separable tetrazole functionality would be to prepare block copolymers with extractable segments such as exemplified below by the preparation of copolymers with a short PAN segment and with a PEG segment, this would allow a reaction to be conducted in one medium then the tetrazole functional material could be removed by extraction with a solvent for the attached polymer segment. Other segmented materials that are suitable for selective separation can comprise segments with dimethylacrylamide/butyl acrylate (DMAA/BA), with dimethylaminoethyl methacrylate (DMAEMA) and with diethyl acrylamide (DEAA), or with NIPAM which can be prepared by another CRP; RAFT.

A further process that would assist in the preparation and purification of bio-responsive products would be to attach the tetrazole functionality to a support with a cleavable functional group and once the sequence of DNA had formed the polymer could be selectively cleaved from the support prior to deprotection.

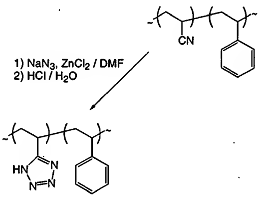
A further use for block copolymers with tetrazole functionality would be the formation of coatings or free standing films wherein the isolated tetrazole segments could form iron (II) complexes that could undergo separate spin-spin transitions under stimulation thereby storing information.

Another use for polymers, particularly dendritic or hyperbranched polymers with attached tetrazole functionality would be to use such a system for solid explosives. Such a material with high concentration of tetrazole functionality could be prepared by synthesis or a normal or hyperbranched polyacrylonitrile-Br polymer followed by

conversion of the acrylonitrile functionality to tetrazole functionality and the bromo-functionality to azide.

DISCUSSION OF EXAMPLES

Block copolymers of styrene and acrylonitrile were synthesized, halogen exchange should be used to prepare well defined polyacrylonitrile blocks from a polystyrene macroinitiator, and the nitrile groups were modified to tetrazole units using the chemistry shown in scheme 1.



Scheme 1. Chemical modifications of the nitrile group in copolymers of Sty and AN

The ionomers with random or blocky structures containing amino and tetrazole groups were studied for aggregation in solution, complex-formation, and morphology. The tetrazole-containing polymers will be tested as materials for the synthesis of DNA.

Other polyacrylonitrile block copolymers that were converted to polytetrazole block copolymers were linear block copolymers with polyethylene oxide and star block copolymers with polybutyl acrylate core.

The nitrile groups of styrene-acrylonitrile based copolymers were successfully transformed to tetrazole units by the reaction with zinc chloride and sodium azide in DMF. The ionomer initially obtained, using published procedures or indeed an even greater excess of sodium azide, up to 2:1 ratio, still contained acrylonitrile units (see the NMR spectrum in Figure 1), but had drastically different properties from the starting material; it dissolved in methanol and swelled in water. Increasing the molar ratio of sodium azide to nitrile units above the ratio of 1:1.3 used earlier provided (co)polymers with complete conversion of the nitrile unit to tetrazole.

EXAMPLES

Preparation of copolymers of acrylonitrile with controlled molecular weight, topology and functionality and their chemical modification to polytetrazole containing materials

1. Conversion of the nitrile groups in a SAN copolymer to tetrazole units (run I.D. nvt-tetrazole5).

The procedure given here gave the best results.

2.79 g (0.3 mmol, corresponding to ca. 0.012 mol of nitrile groups) of a styrene/acrylonitrile copolymer (SAN28 M_n = 9260 g/mol, PDI = 1.14) was dissolved in 10 ml of DMF. 1.56 g (0.024 mol) of sodium azide and 3.27 g (0.024 mol) of zinc chloride were then added and the mixture was stirred at 100°C for 24 h. After about 4 h, the salts had almost completely dissolved. A mixture of 200 ml of water and 15 ml of concentrated hydrochloric acid was separately prepared. 2 ml of this mixture was added

to the reaction mixture (the latter had been cooled down to 60°C), and the obtained suspension of polymer was stirred at 60°C for 2 h. The polymer was then precipitated in the same dilute hydrochloric acid. The obtained suspension was stirred at room temperature overnight. The filtered polymer was washed with water and methanol on the filter. It was then dissolved in DMF (20 ml), and the turbid mixture was poured in the same amount of dilute HCl as before. The polymer was filtered, washed with water and methanol, and dried. These purification steps are necessary to remove the inorganic salts (especially the zinc salts which hydrolyse forming products insoluble in water but soluble in HCl). Finally, the polymer was dissolved in 15 ml of acetone, filtered and precipitated in 200 ml of water. After cooling the suspension in a fridge, it was filtered and the polymer was dried. It was analyzed by IR spectroscopy (film from chloroform on a NaCl plate). All characteristic peaks of poly(5-vinyltetrazole were observed; see Figure 2). The spectrum of poly(5-vinyltetrazole) has been studied (Kruglova, V. A. et al., Vysokomol. Soed. B, 29, 416 (1987)) and it shows the same bands. It should be noted that the band of the nitrile group did not completely disappear in the prepared polytetrazole, but it is known that even at degrees of tetrazolation of PAN as high as 95%, this band is still observed. (Gaponik, P. N., Angew. Makromol. Chem., 219, 77-88 (1994))

These terazolation reactions on SAN copolymers yielded a methanol-soluble polymer of high tetrazole content, as judged from IR analysis. The copolymer was characterized by ^{13}C NMR spectroscopy (Figure 1). The peak at 157 ppm belongs to the carbon atom from the tetrazole ring, and this at 120 ppm corresponds to the nitrile carbon atom. The tertiary carbon atom of polysturene resonates at 145-148 ppm. The carbon

atoms of the macrochain of poly(5-vinyltetrazole) absorb at 37-38 ppm (the peaks of these from PAN are situated at 27-28 ppm and from polystyrene – at 40-48 ppm). One can evaluate that the degree of tetrazolation is around 70%. This is a very high conversion, since even for homo polyAN the tetrazolation is reported to rarely exceed 60-70%. (Note however the conditions developed for the following reactions where complete conversion was attained.)

2. Synthesis of block (co)polymers containing tetrazole groups by ATRP

Previously, (example 1) the reaction of pAN-containing copolymers with sodium azide and zinc chloride in DMF demonstrated this approach to convert the nitrile groups to tetrazole moieties. However, even when using 2 equivalents of azide and 2 equivalents of $ZnCl_2$ vs. each CN group was not sufficient for a complete conversion. (Prior art had employed various ratio's up to 1:1.3)

Two different block copolymers of styrene and acrylonitrile were prepared. They had the composition $Sty_{190}AN_{38}$ and $Sty_{190}AN_{10}$. They were converted to tetrazole-containing copolymer by the reaction with excess molar levels of sodium azide in the presence of zinc chloride.

2a. Diblock copolymers of styrene and acrylonitrile using halogen exchange (run I.D. nvt-Sty-b-AN3 and 4)

6.93 g of a pStyBr macroinitiator (Mn = 19800 g/mol) was dissolved in a mixture of 14 ml of DMF and 10.5 ml of AN added. The catalyst complex for the ATRP consisted of 0.035 g CuCl and 0.109 g bpy. The polymerizations were performed at 80°C. The results are presented in Table 1.

Table 1 Preparation of poly(styene-b-acrylonitrile) copolymers

Entry	Time of pzn, min	Conv (GC)	Mn, g/mol (GPC, conv., and NMR) [DP of AN block by NMR]	PDI
Sty-b-AN3	90	0.140	31400, 21700, 21200 [36]	1.16
Sty-b-AN4	25	0.052	25800, 20500, 20400 [10]	1.13

As is the case with other copolymers with pAN blocks, (US Application No. 10/118,519) the MW determined by GPC in DMF significantly overestimates the true MW of the polyacrylonitrile segment. The two copolymers with pAN blocks of DP = 10 and 38 were used for the preparation of the corresponding block-tetrazoles and block-amines copolymers. The micellular association of these block copolymers in solution will be studied, as well as using them as a template for absorption of metal ions.

2b. Peparation of tetrazole containing block copolymers from diblock copolymers of Sty and AN (Sty-b-AN3 [DP of AN = 36] and Sty-b-AN4 [DP of AN = 10]

The block copolymers of styrene and acrylonitrile prepared above, (they had the composition $Sty_{190}AN_{38}$ and $Sty_{190}AN_{10}$) were reacted with 4 equivalents of the salts and the reaction was complete in ca. 50 hours.

2b1. (run I.D. nvt-tetrazole7) 2.5 g (4 mmol of nitrile groups) of the polymer Sty-b-AN3 was dissolved in 10 ml of DMF. 1.04 g (16 mmol) of sodium azide and 2.18 g (16 mmol) of anhydrous zinc chloride were added and the mixture was heated (using a reflux condenser) to 120°C for 50 h. Then it was cooled down to 60°C and 2 ml of HCl (1:10 by volume in water) was added. The mixture was stirred for 2 hours and the

polymer was precipitated in 200 ml (1:10) HCl. Based on IR spectral analysis, almost complete conversion of nitrile groups to tetrazole units took place.

2b2. (run I.D. nvt-tetrazole8) Preparation of poly(styrene-b-vinyltetrazole) copolymers from a block copolymer of AN

2.5 g (1.23 mmol of nitrile groups) of the polymer Sty-b-AN4 was dissolved in 10 ml of DMF. 0.32 g (4.9 mmol) of sodium azide and 0.67 g (4.9 mmol) of anhydrous zinc chloride were added and the mixture was heated (using a reflux condenser) to 120°C for 50 h. Then it was cooled down to 60°C and 2 ml of HCl (1:10 by volume in water) was added. The mixture was stirred for 2 hours and the polymer was precipitated in 200 ml (1:10) HCl. Based on IR spectral analysis, almost complete conversion of nitrile groups to tetrazole units took place.

A segmented block copolymer with aligned tetrazole functionality of degree of polymerization close to ten is expected to provide a molecularly isolated complex with Fe(II) complexes that will display spin-spin transitions under stimulation thereby storing information at the molecular level. The presence of a polystyrene block will allow the formation of coherent coatings or free standing films. Other segments can also be employed.

3. Synthesis of AN-BA diblock copolymer (run I.D. nvt-anba27)

Firstly, a pBA-based macroinitiator was prepared by the ATRP of BA (50 ml, with added 2 ml of diphenyl ether) in the presence of CuBr (0.0784 g) / PMDETA (112 μl) complex, initiated by MBP (64 μl). The polymerization was carried out at 70°C for 23.5 h (conversion by GC was 62.7%). The product was dissolved in ca. 300 ml of THF

and the copper complexes were removed by passing the solution through a column filled with neutral alumina. The solvent was then evaporated. Mn = 68.7 kg/mol, PDI = 1.09 (pSty standards).

17.66 g of the macroinitiator was dissolved in a mixture of 50 ml of AN and 20 ml of DMF. The chain-extension was catalyzed by CuCl / bpy. The reaction was carried out at 70°C for 21.5 h. The polymer was precipitated in methanol, and analyzed by GPC: Mn = 92.4 kg/mol, PDI = 1.18 (pSty standards).

This result proves the earlier observations that DMF is the solvent of choice for the preparation of acrylonitrile copolymers of high molecular weight. This copolymer had a cylindrical morphology.

4. Tethered tetrazole (co)polymers

A polyacrylonitrile homopolymer and a styrene/acrylonitrile copolymer both attached to silica particles were also converted to tetrazoles. Based on IR spectral analysis, no unreacted nitrile groups was left in the samples.

The general procedure was the following. The measured amount of the tethered (co)polymer was dissolved in DMF, and NaN_3 and anhydrous $ZnCl_2$ (4 equivalents vs. CN) were added. The mixture was stirred at 120°C for 50 h. Then it was cooled down to 60°C and a solution of HCl (1:10 in water) was added. The reaction mixture was stirred at this temperature for 3-5 h, and the product was precipitated in large excess of the same HCl solution. The polymer was stirred with the HCl overnight at room temperature, filtered, washed on the filter with the same HCl solution and then with water and dried. Experimental details are summarized in Table 2.

Table 2. Tetrazolation reactions

Experiment	Polymer	Reagents	HCl (1:10)	Properties
Nvt-ttrzl9	SAN-SiO_2 (L.B.) - 1.4 g (0.006 mol CN) in 10 mL DMF	1.56 g NaN_3 and 3.27 g $ZnCl_2$ (0.024 mol)	2 mL; 5 h at 60°C	-
Nvt-ttrzl10	PAN1ttrzl (Mn (GPC) = 39540 g/mol, PDI = 1.08), 1.06 g (0.02 mol CN) in 20 mL DMF	5.2 g NaN_3 and 10.9 g $ZnCl_2$ (0.08 mol)	15 mL; 3 h at 60°C (brown solution forms)	Sol. DMF (heating), aq. NaOH; insol. H_2O, MeOH, acetone
Nvt-ttrzl11	SAN34 (Mn = 8460 g/mol, PDI = 1.08), 2.79 g (0.012 mol CN) in 20 mL DMF	3.12 g NaN_3 and 6.54 g $ZnCl_2$ (0.048 mol)	10 mL; 4 h at 60°C (in ca. 1 h, solution forms)	Sol. MeOH, aq. NaOH, acetone

The IR spectra of the starting nitrile-containing polymers and the tetrazoles prepared therefrom are shown in Figure 3. As can be seen from the spectra, the nitrile groups were completely converted to tetrazole functionality.

CLAIMS

1. A poly(5-vinyltetrazole) with a molecular weight distribution less than 2.0

2. A copolymer comprising 5-vinyltetrazole units a molecular weight distribution less than 2.0.

3. A block copolymer comprising a poly(5-vinyltetrazole) segment.

4. A multisegmented block copolymer comprising distributed poly(5-vinyltetrazole) segment.

5. A star block copolymer comprising poly(5-vinyltetrazole) segments.

6. A brush copolymer comprising poly(5-vinyltetrazole) segments.

7. A (co)polymer comprising poly(5-vinyltetrazole) tethered to a surface.

8. A block (co)polymer comprising poly(5-vinyltetrazole)segments tethered to a surface.

9. The homopolymer of claim 1, wherein the polymer is a linear, branched, hyperbranched or dendritic polymer.

10. The copolymer of claim 2, wherein the polymer is a linear, branched, hyperbranched or dendritic polymer.

11. The copolymer of claim 10, comprising radically copolymerizable monomer(s)

12. The block copolymer of claim 3, wherein the other segment(s) comprise radically copolymerizable monomer(s)

13. A process for the conversion of attached nitrile functionality whereby the ratio of sodium azide and zinc chloride to each attached nitrile functionality is greater than 1.5.

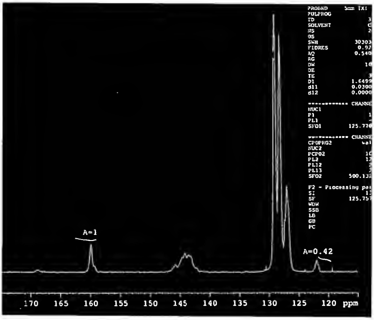


Figure 1. NMR spectrum of copolymer formed after tetrolization of a styrene acrylonitrile copolymer

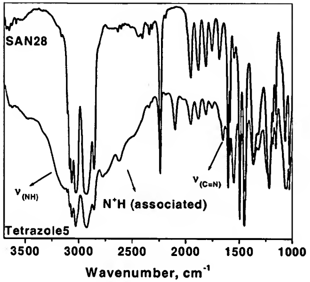


Figure 2. IR spectra (films from chloroform on a NaCl plate) of SAN copolymer and the product of its tetrazolation. Note the presence of a new band at 1653 cm^{-1} as well as the broad band (2800-2300 cm^{-1}) corresponding to associated NH bonds.

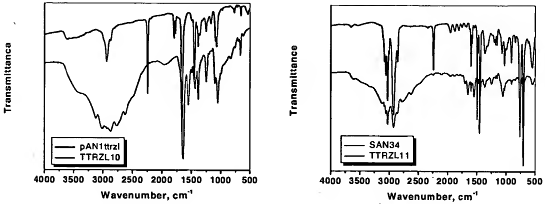


Figure 3. Convertion of the nitrile groups in a SAN copolymer to tetrazole units. Spectra were obtained from films cast from acetone (SAN34 and TTRZL11) or DMF (PAN1ttrzl and TTRZL10) onto KBr plates.